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04 Ionic Equilibrium

Introduction

The study of ionic reactions at equilibrium is known as ionic equilibrium

According to Conductivity Substances are of two Types

(1) Non-Conductor - Those substances which do not show the flow of current or electricity.

Ex. Non - metals, plastics, rubber, wood etc.

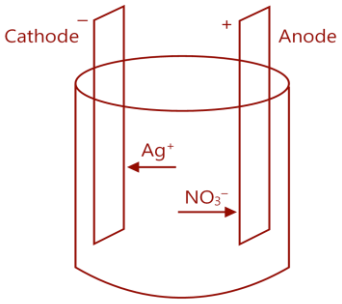
Exception – Graphite is a non-metal but shows conductivity due to motion of free electrons.

(2) Conductors – Those substances which show conductivity or flow of current are called conductors and these are of two types:

(a) Metallic conductors – Those conductors which show conductivity due to motion of free electrons.

Ex. All metals

(b) Ionic conductors –



Those conductors which show conductivity due to movement of free ions. Ions are in free state in the solutions of ionic compounds. On passing electric current through the solution, ions move towards oppositely charged electrodes, i.e., the cation moves towards cathode (negative electrode) and the anion moves towards anode (positive electrode). Due to this reason, they are called as cations and anions respectively. The current flows through the solution due to the movement of the ion.

According to Strength, Ionic Conductors Can be Classified as –

(1) Strong electrolytes – Those ionic conductors which are almost **completely ionized in aqueous solution** are called as strong electrolytes.

For strong electrolytes, the value of degree of ionisation is almost 100% i.e. $\alpha = 1$

Ex.

(a) All Strong Acids : H_2SO_4, HCl, HNO_3, $HClO_4$, HBr, HI

(b) All Strong Bases : KOH, NaOH, $Ba(OH)_2$, CsOH, RbOH

(c) All Ionic Salts : NaCl, KCl, $CuSO_4$ etc.

(2) Weak electrolytes – Those electrolytes which are **partially ionized in aqueous solution** are called as weak electrolytes. For weak electrolytes the value of α is less than one.

Ex.

(a) All Weak acids : HCN, CH_3COOH, HCOOH, H_2CO_3, H_3PO_3, H_3PO_2, $B(OH)_3$ or H_3BO_3, etc.

(b) All Weak bases : NH_4OH, $Cu(OH)_2$, $Zn(OH)_2$, $Fe(OH)_3$, $Al(OH)_3$ etc.

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Arrhenius Concept

(a) According to Arrhenius, when an electrolyte dissolves in water, it splits up into two oppositely charged particles i.e. cation and anion.

(b) In an electrolytic solution (aqueous solution of electrolyte), total +ve charge = total –ve charge i.e. solution is electrically neutral.

In an electrolytic solution number of +ve ions may or may not be equal to the number of negative ions.

(c) Properties of an electrolytic solution are defined by its ions.

Ex. Blue colour of $CuSO_4$ solution is due to Cu^{+2} ions (dark blue colour)

(d) When electric current is passed through aqueous solution of an electrolyte then cation shows migration towards cathode where as anion shows migration towards anode.

(e) When a weak electolyte is dissolved in water an equilibrium is set up between unionized species and ionized species.

This condition of the reversible ionic reaction is known as ionic equilibrium.

$AB\ (aq.) \rightleftharpoons A^+\ (aq.) + B^-\ (aq.)$

According to Law Of Mass Action.

$$K = \frac{[A^+][B^-]}{[AB]}$$

K = Ionisation Constant

Illustration 1:

No. of total ions and resultant total charge in A_2B_3 electrolyte:

(1) Five and + 1 (2) Five and – 1 (3) 0 and 0 (4) None of them

Solution:

(4)

Illustration 2:

Assertion: H_2SO_4 is a strong acid.

Reason: H_2SO_4 is almost completely ionised in aqueous solution.

(1) A (2) B (3) C (4) D

Solution:

(1)

Ostwald's Dilution Law

⇒ Ostwald was the first to apply law of mass action to ionic equilibrium.

⇒ Ostwald dilution law is applicable only for weak electrolytes.

Statement:

According to Ostwald's dilution law when solution of a weak electrolyte is diluted then the degree of ionization of weak electrolyte increases, and at infinite dilution it remains 100% dissociated.

Let	$AB(aq) \rightleftharpoons A^+(aq) + B^-(aq)$		
Initial concentration	C	0	0
At Equilibrium	$(C - C\alpha)$	$(C\alpha)$	$(C\alpha)$

α = Degree of Ionization

According to LOMA : $K = \frac{[A^+][B^-]}{[AB]} \Rightarrow K = \frac{C\alpha \times C\alpha}{C(1-\alpha)} = \frac{C\alpha^2}{(1-\alpha)}$

If $\alpha <<<< 1$ then $1 - \alpha \approx 1$

$K = C\alpha^2$ or $\alpha = \sqrt{\frac{K}{C}}$ (K= Constant, at constant temperature)

$\alpha \propto \frac{1}{\sqrt{C}} \Rightarrow \alpha \propto \sqrt{V} \quad \because \left(C \propto \left(\frac{1}{V}\right)\right)$

$\alpha \propto \sqrt{\text{dilution}}$

dilution ↑ α ↑

At infinite dilution, α = 100%

Thus, for weak electrolytes the degree of ionisation is directly proportional to square root of dilution or inversely proportional to square root of concentration. This law is known as Ostwald's Dilution Law.

➢ At infinite dilution the value of α becomes equal to one.

Application of Ostwald's Dilution Law: $\boxed{K = C\alpha^2}$

Application of Ostwald's Dilution Law

- **(a) For mono basic weak acid (HA)**
- **(b) For mono acidic weak base (BOH)**

(a) For mono basic weak acid (HA)

(i)

	HA	⇌	H^+	+	A^-
Initial Concentration	C		0		0
At equilibrium	C – Cα		Cα		Cα

Ionization constant (K_a) α is Degree of Dissociation

$$K_a = \frac{[H^+][A^-]}{[HA]} = \frac{C\alpha \times C\alpha}{C - C\alpha} \Rightarrow K_a = \frac{C^2\alpha^2}{C(1-\alpha)} = \frac{C\alpha^2}{(1-\alpha)}$$

$$\because \alpha <<<< 1 \Rightarrow (1-\alpha) \approx 1 \Rightarrow K_a = C\alpha^2 \Rightarrow \alpha = \sqrt{\frac{K_a}{C}}$$

(ii) $[H^+]$ (Concentration of H^+)

$[H^+] = C\alpha$ .....(1)

$K_a = C\alpha^2$ or $\alpha = \sqrt{\frac{K_a}{C}}$ .....(2)

from Eq. (1) and (2) $[H^+] = C \times \sqrt{\frac{K_a}{C}}$

$[H^+] = \sqrt{K_a \times C}$

(iii) $pH = -\log [H^+]$

put the value of $[H^+]$

$pH = -\log (\sqrt{K_a \times C}) = -\log (K_a \times C)^{1/2}$

$pH = -\frac{1}{2} [\log K_a + \log C]$

$pH = -\frac{1}{2} \log K_a - \frac{1}{2} \log C$

$pH = \frac{1}{2} pK_a - \frac{1}{2} \log C$

Summary:

1. $K_a = C\alpha^2$
2. $[H^+] = C\alpha = \sqrt{K_a \times C}$
3. $pH = -\log [H^+]$

   or $pH = \frac{1}{2} pK_a - \frac{1}{2} \log C$

(b) For mono acidic weak base (BOH)

(i)

	BOH	⇌	B^+	+	OH^-
Initial Concentration	C		0		0
At equilibrium	C – Cα		Cα		Cα

Ionization constant (K_b) α is Degree of Dissociation

$$K_a = \frac{[B^+][OH^-]}{[BOH]} = \frac{C\alpha \times C\alpha}{C - C\alpha} \Rightarrow K_b = \frac{C^2\alpha^2}{C(1-\alpha)} = \frac{C\alpha^2}{(1-\alpha)}$$

$$\because \alpha <<<< 1 \Rightarrow (1-\alpha) \approx 1 \Rightarrow K_b = C\alpha^2 \Rightarrow \alpha = \sqrt{\frac{K_b}{C}}$$

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(ii) $[OH^-]$ (Concentration of OH^-)

$[OH^-] = C\alpha$ .....(1)

$K_b = C\alpha^2$ or $\alpha = \sqrt{\frac{K_b}{C}}$ .....(2)

from Eq. (1) and (2) $[OH^-] = C \times \sqrt{\frac{K_b}{C}}$

$[OH^-] = \sqrt{K_b \times C}$

(iii) $pOH = -\log [OH^-]$

put the value of $[OH^-]$

$pOH = -\log (\sqrt{K_b \times C}) = -\log (K_b \times C)^{1/2}$

$pOH = -\frac{1}{2} [\log K_b + \log C]$

$pOH = -\frac{1}{2} \log K_b - \frac{1}{2} \log C$

$pOH = \frac{1}{2} pK_b - \frac{1}{2} \log C$

Summary:

1. $K_b = C\alpha^2$
2. $[OH^-] = C\alpha = \sqrt{K_b \times C}$
3. $pOH = -\log [H^+]$ or $pOH = \frac{1}{2} pK_b - \frac{1}{2} \log C$

Illustration 3:

Find out the value of α of 10^{-2} M HCN solution if $[H^+] = 10^{-3}$.

Solution:

$[H^+] = C\alpha$

$10^{-3} = 10^{-2} \alpha$ or $\alpha = \frac{10^{-3}}{10^{-2}} = 10^{-1}$ or $\alpha = 0.1$

$\%\alpha = 10\%$

Illustration 4:

For 10 M CH_3COOH solution if $K_a = 10^{-5}$, then, find out:

(1) α (2) $[H^+]$ (3) pH

Solution:

(1) α

(Degree of ionisation) :– $K_a = C\alpha^2$

$10^{-5} = 10\alpha^2$ or $\alpha^2 = \frac{10^5}{10} = 10^{-6}$ or $\alpha = 10^{-3}$

(2) $[H^+] = C\alpha = 10 \times 10^{-3} = 10^{-2}$

(3) $pH = -\log [H^+] = -\log 10^{-2} = 2$

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Illustration 5:

For 10^{-3} M H_2CO_3 if α = 10%, then, find out the value of pH ?

Solution:

Normality = M × V.F. = $10^{-3} \times 2 = 2 \times 10^{-3}$ N

$[H^+]$ = $C\alpha = 2 \times 10^{-3} \times 0.1 = 2 \times 10^{-4}$ N

pH = $-\log [H^+]$

= $-\log (2 \times 10^{-4})$

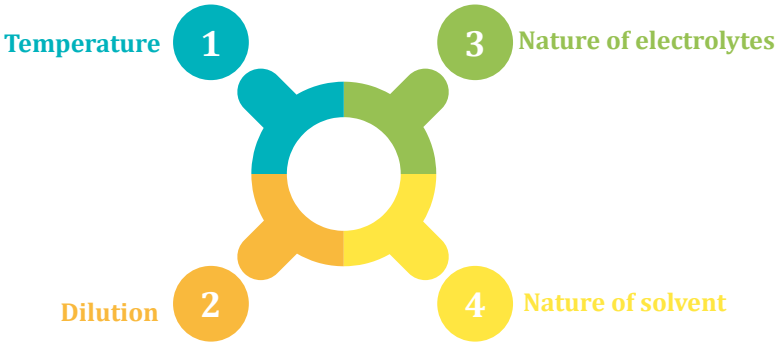
= $-\log 2 - \log 10^{-4}$

= $-0.3010 + 4 = 3.7$

Limitation of Ostwald's Dilution Law:

It is not applicable for strong electrolytes.

Factors affecting the Value of Degree of ionisation



(1) **Temperature** → On increasing temperature, ionization increases, so α increases as dissociation is an endothermic process.

(2) **Dilution** → $\alpha \propto \sqrt{V}$ so on dilution, α increases.

(3) **Nature of electrolytes**

(i) Strong electrolytes
α = 100%

(ii) Weak electrolytes
α < 100%

(4) **Nature of solvent**

If Dielectric constant μ of solvent increases, then the value of α increases.

$H_2O \rightarrow \mu = 81$

$D_2O \rightarrow \mu = 79$

$C_6H_6 \rightarrow \mu = 2.5$

$CCl_4 \rightarrow \mu = 0$

(5) **Mixing of ions**

(a) Common ion effect	(b) Odd ion effect
When a strong electrolyte having a common ion, is mixed with weak electrolyte, then, the degree of ionisation ($\propto$) of weak electrolyte is decreased. This effect is called as the common ion effect.	When a strong electrolyte having an odd ion, is mixed with weak electrolyte, then, the degree of ionisation (α) of weak electrolyte is increased. This effect is called as the odd ion effect.

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Common ion: On mixing CH_3COONa with CH_3COOH solution

Initially $CH_3COOH \rightleftharpoons CH_3COO^- + H^+$

On mixing $CH_3COONa \rightarrow CH_3COO^- + Na^+$

$CH_3COOH \rightleftharpoons CH_3COO^- + H^+$

$[CH_3COO^-]$ increases, so, $[H^+]$ decreases

Odd ion: On mixing, NaOH with CH_3COOH solution

Initially $CH_3COOH \rightleftharpoons CH_3COO^- + H^+$

On mixing, $NaOH \rightarrow Na^+ + \boxed{OH^-}$

$CH_3COOH \rightleftharpoons CH_3COO^- + \boxed{H^+}$

$\rightarrow H_2O$ (due to odd ion effect)

Illustration 6:

Assertion : NaCl + HCl does not experience common ion effect.

Reason : Both NaCl and HCl are strong electrolytes.

(1) A (2) B (3) C (4) D

Solution:

(1)

Illustration 7:

For which of the following electrolytes dilution law is applicable ?

(1) NaCl (SASB salt) (2) HCl (SA)

(3) CH_3COONa (WASB salt) (4) None

Solution:

(4)

Logarithm Basics:-

Formulae:

(i) $\ln x = \log_e x = 2.303 \log_{10} x = 2.303 \log x$ (ii) $\log (x \times y) = \log x + \log y$

(iii) $\log\left(\frac{x}{y}\right) = \log x - \log y$ (iv) $\log x^y = y \log x$

Some values of Log:

log 1 = 0	log 8 = 0.9030
log 2 = 0.3010	log 9 = 0.9542
log 3 = 0.4771	log 10 = 1
log 4 = 0.6020	log 11 = 1.04
log 5 = 0.6989	log 100 = 2
log 6 = 0.7781	log 1000 = 3
log 7 = 0.8451	log 10000 = 4

Some terms which are used in ionic equilibrium :

Antilog: Antilog (x) = 10^x

antilog (0) = $10^0 = 1$

antilog (0.3) = $10^{0.3} = 2$

antilog (0.48) = $10^{0.48} = 3$

antilog (0.6) = $10^{0.6} = 4$

antilog (0.7) = $10^{0.7} = 5$

antilog (0.78) = $10^{0.78} = 6$

antilog (0.85) = $10^{0.85} = 7$

antilog (0.9) = $10^{0.9} = 8$

antilog (0.95) = $10^{0.95} = 9$

antilog (1) = $10^1 = 10$

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Ex. (i) log 6 = log (2 × 3)
= log 2 + log 3
= 0.3010 + 0.4771 = 0.7781
(ii) log 30 = log (3 × 10)
= log 3 + log 10
= log 0.4771 + 1 = 1.4771
(iii) log 1000 = log 10^3
= 3 log 10 = 3 × 1 = 3

Ex. Antilog (2) = 10^2 = 100
Antilog (0.3010) = $10^{.3010}$ = 2
Antilog [log (2)] = Antilog (0.3010) = 2

pH - Scale: Given by – **Sorenson**

pH Scale is called Sorenson scale.

pH scale is a measuring scale used to measure strength of acid and base and its value is equal to – log[H^+]

i.e. $$\mathbf{pH = -\log [H^+] = \log \frac{1}{[H^+]}}$$

Ex. $[H^+] = 10^{-3}$
$pH = -\log 10^{-3} = +3 \log 10 = 3$

Conclusion:

If pH = x then $[H^+] = 10^{-x}$ or Vice versa

i.e. If $[H^+] = 10^{-x}$ then pH = x

pOH → It is equal to – log [OH^-]

i.e. $pOH = -\log [OH^-] = \log \frac{1}{[OH^-]}$

Ex. If $X = \frac{a}{b} \times 10^{-c}$, then find pX?

Sol. $pX = -\log X = -\log \left(\frac{a}{b} \times 10^{-c}\right)$

$pX = -\left[\log \frac{a}{b} + \log 10^{-c}\right] = -[\log a - \log b - c]$

$$\boxed{pX = c + \log b - \log a}$$

pH scale at 25ºC

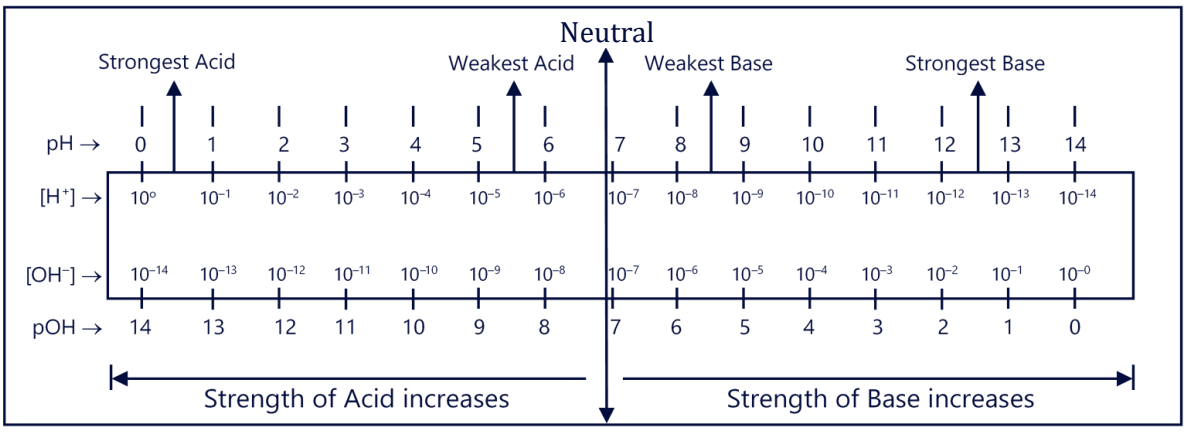

Illustration 8:

If $[H^+] = \frac{5}{3} \times 10^{-4}$ then find pH ?

Solution:

$pH = -\log [H^+] = -\log\left(\frac{5}{3}\times 10^{-4}\right)$

$= -\left[\log\frac{5}{3} + \log 10^{-4}\right] = -[\log 5 - \log 3 - 4]$

$= -[0.699 - 0.4771 - 4] = -[-3.778] = 3.778$

Explanation of Water

a. Nature of water is neutral. **$[H^+] = [OH^-] = 10^{-7}$M (At 25°C)**

i.e. Nature of water is **Neutral**.
At 25°C $\Rightarrow$ pH = 7 & pOH = 7 $\Rightarrow$ pH = pOH

b. No. of moles of H_2O in 1 litre water $= \frac{1000}{18} = 55.5$ moles

c. Molar concentration of $H_2O = 55.5$ mol L^{-1}

d. Number of H_2O molecules in 1 litre water = 55.5 N_A (N_A= Avogadro's Number)

e. Concentration of H^+ and OH^- ions in 1 litre water

$[H^+] = 10^{-7}$ mol L^{-1} and $[OH^-] = 10^{-7}$ mol L^{-1}

f. No. of H^+ and OH^- ions in 1 litre water

No. of H^+ ions = $10^{-7} N_A$ and No. of OH^- ions = 10^{-7} N_A

g. In water (Number of H_2O molecules : Number of H^+ ions)

$= 55.5\ N_A : 10^{-7}\ N_A$

$= 55.5 \times 10^7 : 1$

i.e. one H^+ ion is obtained from 55.5×10^7 Number of H_2O molecules

h. Degree of ionisation of water (α):

Let	**$H_2O(aq)$**	**$\rightleftharpoons$**	**$H^+(aq)$**	**+**	**$OH^-(aq)$**
Initial concentration	**C**		**0**		**0**
At Equilibrium	**(C – Cα)**		**(Cα)**		**(Cα)**

$\Rightarrow [H^+] = C\alpha$

$\Rightarrow \alpha = \frac{10^{-7}}{55.5} = 1.8 \times 10^{-9}$ **$\%\alpha = 1.8 \times 10^{-7}\%$**

Hence, water is a very weak electrolyte.

i. K (Ionisation constant of water):

$$H_2O \rightleftharpoons H^+ + OH^-$$

$$K = \frac{[H^+][OH^-]}{[H_2O]}$$

$$K = \frac{10^{-7} \times 10^{-7}}{55.5} \text{ or } \boxed{K = 1.8 \times 10^{-16}}$$

j. Ionic product of water K_w:

$$H_2O\,(aq) \rightleftharpoons H^+\,(aq) + OH^-\,(aq)$$

$$K = \frac{[H^+][OH^-]}{H_2O} \Rightarrow K \times [H_2O] = [H^+]\,[OH^-]$$

Since, dissociation takes place to a very small extent, $[H_2O]$ may be regarded as constant.

Thus, the product gives another constant which is designated as K_w.

$$\boxed{K_w = [H^+][OH^-]}$$

At 25°C : $K_w = 10^{-7} \times 10^{-7} = 10^{-14}$

$K[H_2O] = K_w \Rightarrow \boxed{K_w > K}$ (always)

Various forms of K_W

(1) $K_W = [H^+]\,[OH^-]$ for water $[H^+] = [OH^-]$

(2) $K_W = [H^+]^2$

(3) $K_W = [OH^-]^2$

(4) $K_W = [H_3O^+]\,[OH^-]$

(e) $K_W = [H_3O^+]^2$ {$[H_3O^+]$ = $[H^+]$}

Hydronium ion Proton

- **Relation between pH and pOH :**

$K_W = [H^+]\,[OH^-]$

Taking – log on both sides

$-\log K_W = -\log [H^+] - \log [OH^-]$

$$\boxed{pK_w = pH + pOH}$$

- **Nature of water is neutral so,**

$[pH = pOH]$

$pK_w = pH + pH$ | $pK_w = pOH + pOH$

$2pH = pK_w$ | $2\,pOH = pK_w$

$pH = \frac{pK_w}{2}$ | $pOH = \frac{pK_w}{2}$

$$\boxed{pH = pOH = \frac{pK_W}{2}}$$

At 25°C, $K_W = 10^{-14}$ or $pK_W = 14$

$\therefore$ $pH + pOH = 14$ or $pH = pOH = 7$

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k. Effect of temperature:

$$H_2O \rightleftharpoons H^+ + OH^- \qquad \Delta H = +ve$$

Ionization of water is as endothermic process, so, on increasing temperature α increases or $[H^+]$ and $[OH^-]$ increases or $[H^+]\,[OH^-]$ increases i.e. K_w increases, it means pH decreases or pOH decreases.

On increasing ↑ T ⇒ α Increases ↑ ⇒ $[H^+]$ ↑ & $[OH^-]$ ↑ ⇒ K_w ↑

K_w ↑ ⇒ pK_w ↓ ⇒ pH ↓ & pOH ↓

At 25°C, $K_w = 10^{-14}$

At 90°C, $K_w = 10^{-12}$

	At 25°C	At 90°C
K_W	10^{-14}	10^{-12}
pK_w	14	12
pH = pOH	7	6
$[H^+] = [OH^-] = \sqrt{K_W}$	10^{-7}	10^{-6}
$pH + pOH = pK_W$	14	12

★ Golden Key Points ★

- On increasing temperature, both $[H^+]$ and $[OH^-]$ increases equally so water remains neutral but pH changes from 7 to 6 at 90°C.

Illustration 9:

Dissociation constant of water at 25° C is

(1) $10^{-14} \times (55.5)^{-1}$ (2) $10^{-7} \times (18)^{-1}$ (3) $10^{-14} \times (18)^{-1}$ (4) $10^{-7} \times (55.4)^{-1}$

Solution:

(1)

Illustration 10:

What should be the number of H^+ ions in 1 mL of distilled water, if the number of H^+ ions in 1 L is 6.023×10^{16}?

Solution:

Number of H^+ ions in 1 mL distilled water = $\frac{6.023\times10^{16}}{1000} = 6.023\times10^{13}$

Illustration 11:

Calculate the sum of $[H^+]$ & $[OH^-]$ present in pure water at 25°C

Solution:

At 25°C, pH =pOH =7 for pure water.

$[H^+] = 10^{-7}M$, $[OH^-] = 10^{-7}M$

$\therefore$ $[H^+] + [OH^-] = 10^{-7} + 10^{-7} = 2 \times 10^{-7}M$

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Illustration 12:

At a 25°C temperature, pH of pure water is found to be 4. Determine pK_w at the same temperature.

Solution:

For pure water

$[H^+] = 10^{-7}M$

$pH = pOH = \frac{pK_w}{2}$

$\therefore \quad pK_w = 2pH = 2 \times 4 = 8$

C. Conjugate acid-base pair:

(i) If two species differ only by one H^+ ion then they form conjugate acid-base pair.

(ii) When an acid loses a proton, the residual part of it has a tendency to regain a proton. Therefore it behaves as a base.

$CH_3COOH \rightleftharpoons CH_3COO^- + H^+$

Weak acid ($K_a = 1.85 \times 10^{-5}$) — Conjugate strong base or acceptor ion

$NH_4OH + H^+ \rightleftharpoons NH_4OH_2^+ \longrightarrow NH_4^+ + H_2O$

Weak base ($K_b = 1.85 \times 10^{-5}$) — Conjugate strong acid (acceptor ion)

$HCl \longrightarrow H^+ + Cl^-$

Strong acid ($K_a \simeq \infty$) — Conjugate weak base (spectator ion) Accepting tendency of $H^+ \simeq 0$

$NaOH + H^+ \longrightarrow NaOH_2^+ \longrightarrow Na^+ + H_2O$

Strong base ($K_b \simeq \infty$) — Conjugate weak acid (spectator ion)

Note : Strong acids have weak conjugate bases while weak acids have strong conjugate bases. Similarly, strong bases have weak conjugate acids while weak bases have strong conjugate acids.

D. Relation between conjugate acid-base pair :–

Example –

$CH_3COOH \rightleftharpoons CH_3COO^- + H^+$

Acid — conjugate base

$NH_4OH \rightleftharpoons NH_4^+ + OH^-$

Base — conjugate acid

CH_3COOH	CH_3COO^-
acid	conjugate base
$CH_3COOH + H_2O \rightleftharpoons CH_3COO^- + H_3O^+$	$CH_3COO^- + H_2O \rightleftharpoons CH_3COOH + OH^-$
$K_a = \frac{[CH_3COO^-][H_3O^+]}{[CH_3COOH]}$ ..... (i)	$K_b = \frac{[CH_3COOH][OH^-]}{[CH_3COO^-]}$ ..... (ii)

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In both the reactions H_2O is in excess quantity so active mass of H_2O is one.

Now multiply the equation (i) and (ii) $K_a \times K_b = [H^+]\,[OH^-]$

we know $[H^+] \times [OH^-] = K_W$ (Ionic product of water) $\boxed{K_a \times K_b = K_w}$

Taking –log on both sides $\boxed{pK_a + pK_b = pK_w}$

we know that for water at 25°C, $K_W = 10^{-14}$ or $pK_W = 14$

So $\boxed{K_a \times K_b = 10^{-14}}$

or $\boxed{pK_a + pK_b = 14}$

Above relation is applicable only for conjugate acid-base pairs.

Illustration 13:

Determine the ionisation constant of CH_3COOH, if K_b for CH_3COO^- at 25°C is 5×10^{-10}.

Solution:

$(K_b)_{CH_3COO^-} = 5 \times 10^{-10}$

$(K_a)_{CH_3COOH} = ?$

$(K_a)_{CH_3COOH} \times (K_b)_{CH_3COO^-} = K_w$

$\Rightarrow$ K_w at 25°C $= 10^{-14}$

$(K_a)_{CH_3COOH} = \dfrac{10^{-14}}{5 \times 10^{-10}} = 0.2 \times 10^{-4} = 2 \times 10^{-5}$

Illustration 14:

Calculate following values at 25°C for given species:

(i) pK_a of H_3O^+ **(ii) pK_b of OH^-**

Solution:

(i) pK_a of $H_3O^+ \Rightarrow$ conjugate base of H_3O^+ is H_2O

$(K_b)_{H_2O}$ = Ionisation constant of water

$(K_b)_{H_2O} = 1.8 \times 10^{-16}$

$(pK_b)_{H_2O} = 16 - \log 1.8 = 16 - 0.24 = 15.76$

$(pK_a)_{H_3O^+} + (pK_b)_{H_2O} = 14$ at 25°C

$\therefore$ $(pK_a)_{H_3O^+} = 14 - 15.76 = -1.76$

(ii) pK_b of $OH^- \Rightarrow$ conjugate acid of OH^- is H_2O

$(pK_a)_{H_2O} + (pK_b)_{OH^-} = 14$ at 25°C

$(pK_b)_{OH^-} = 14 - 15.76 = -1.76$

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pH of mixture of acid and base.

(a) pH of mixture of strong acids:

$N_1V_1 + N_2V_2 + N_3V_3 + \ldots\ldots\ldots\ldots = NV$

V = Volume of final solution $= V_1 + V_2 + V_3 + \ldots\ldots\ldots$

N = Normality of final solution $= [H^+]$ in final solution.

(b) pH of mixture of strong bases:

$N_1V_1 + N_2V_2 + N_3V_3 + \ldots\ldots\ldots\ldots = NV$

V = Volume of final solution $= V_1 + V_2 + V_3 + \ldots\ldots\ldots$

N = Normality of final solution $= [OH^-]$ in final solution.

(c) pH of mixture of strong acids and strong bases :

For acid :

$N_1V_1 + N_2V_2 + N_3V_3 + \ldots\ldots\ldots\ldots = (NV)_{Acid}$

For base :

$N_1V_1 + N_2V_2 + N_3V_3 + \ldots\ldots\ldots\ldots = (NV)_{Base}$

(i) If

$(NV)_{Acid} > (NV)_{Base}$ then solution is acidic.

$NV = (NV)_{Acid} - (NV)_{Base}$ and

$[H^+] = N$

(ii) If

$(NV)_{Base} > (NV)_{Acid}$ then solution is basic.

$NV = (NV)_{Base} - (NV)_{Acid}$ and

$[OH^-] = N$

(iii) If,

$(NV)_{acid} = (NV)_{base}$ then solution is neutral.

Illustration 15:

Calculate the pH of the following aqueous solutions at 25°C containing the mixture of -

(a) 2 mol H_2SO_4 and 1 mol HNO_3 in 10 L aqueous solution

(b) 4 g NaOH and 5.6 g KOH mixed in 20 L aqueous solution

Solution:

(a) $[H^+] \frac{2\times2+1\times1}{10} = 0.5 = \frac{1}{2}$

$pH = -\log 2^{-1} = 0.3$

(b) $[OH^-] = \frac{\frac{4}{40}+\frac{5.6}{56}}{20} = 10^{-2}$

$pOH = 2$

$pH = 12$

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Illustration 16:

4 L of 0.1 M Ba $(OH)_2$ and 6 L of 0.05 M NaOH are mixed together. Determine the pH of the resultant mixture at 25°C.

Solution:

$$[OH^-] = \frac{N_1V_1 + N_2V_2}{V}$$

$$= \frac{0.1 \times 2 \times 4 + 0.05 \times 6}{10}$$

$$= \frac{0.8 + 0.3}{10} = 1.1 \times 10^{-1}$$

pOH $= -\log(1.1 \times 10^{-1})$

$= 1 - \log 1.1 \approx 0.97$

pH $= 14 - 0.97 = 13.3$

Illustration 17:

Calculate the pH of mixture formed by mixing:

(a) 100 ml of 0.1M HNO_3 + 900 ml of 0.1 M HCl.

(b) Equal volumes of 0.2M HCl, 0.1 M H_2SO_4 & 0.2M $HClO_4$.

Solution:

(a) $$[H^+] = \frac{0.1 \times 0.1 + 0.9 \times 0.1}{1} = \frac{10^{-2} + 9 \times 10^{-2}}{1}$$

$[H^+] = 10^{-1}$; pH $= -\log(10^{-1}) = 1$

(b) $$[H^+] = \frac{0.2 \times V + 0.1 \times 2 \times V + 0.2 \times V}{3V} = \frac{0.6 \times V}{3V} = 2 \times 10^{-1}$$

pH $= -\log(2 \times 10^{-1}) = 1 - 0.3 = 0.7$

Illustration 18:

4 L of 0.2 M HNO_3 and 6 L of 0.1 M NaOH are mixed at 25°C. Determine the pH of the resultant mixture.

Solution:

gm-eq. of HNO_3 $= M \times VF \times V_{(L)}$

$= 0.2 \times 1 \times 4 = 0.8$

gm-eq. of NaOH $= M \times VF \times V_{(L)}$

$= 0.1 \times 1 \times 6 = 0.6$

gm-eq. of acid > gm. Eq. of base

$\Rightarrow$ $[H^+] = \frac{0.8 - 0.6}{10} = 0.02 = 2 \times 10^{-2}$

$\Rightarrow$ pH $= -\log(2 \times 10^{-2}) = 2 - \log 2 = 2 - 0.3 = 1.7$

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BEGINNER'S BOX-1

1. The pH of a 0.005 M H_2SO_4 solution is–

(1) 3.3 (2) 5.0 (3) 2.0 (4) 4.0

2. If pure water has pK_w =13.36 at 50ºC, the pH of pure water will be–

(1) 6.68 (2) 7.0 (3) 7.13 (4) 6.0

3. How many H^+ ions are present in 1 ml of a solution whose pH is 13 ?

(1) 10^{-16} (2) 6.022×10^{13} (3) 6.022×10^{7} (4) 6.022×10^{23}

4. The pH of solutions A, B, C and D are 9.5, 2.5, 3.5 and 5.5 respectively. The most acidic solution is–

(1) D (2) C (3) A (4) B

5. Calculate the concentration of the formate ion present in 0.100 M formic acid (HCOOH) solution at equilibrium ($K_a = 1.7 \times 10^{-4}$).

(1) 4.1×10^{-3} M (2) 3.1×10^{-3} M

(3) 2.1×10^{-3} M (4) 5.1×10^{-3} M

6. Which of the following is the weakest acid ?

(1) Phenol ($K_a = 1.3 \times 10^{-10}$) (2) Hydrocyanic acid ($K_a = 4.9 \times 10^{-10}$)

(3) Acetic acid ($K_a = 1.8 \times 10^{-5}$) (4) Benzoic acid ($K_a = 6.5 \times 10^{-5}$)

7. The pH of 0.1 M monobasic acid is 4.50. The acidity constant (K_a) of the monobasic acid is–

(1) 1.0×10^{-7} (2) 1.0×10^{-5} (3) 1.0×10^{-4} (4) 1.0×10^{-8}

8. Which of the following is the strongest base ?

(1) $C_6H_5NH_2$ ($pK_b = 9.42$) (2) $C_6H_5NHCH_3$ ($pK_b = 9.15$)

(3) $C_6H_5N(CH_3)_2$ ($pK_b = 8.94$) (4) $C_6H_5NHC_2H_5$ ($pK_b = 8.89$)

9. Value of dissociation constant of acetic acid is 10^{-6}, where as dissociation constant of formic acid is 10^{-5}. find the value of pK_a (acetic acid) - pK_a (formic acid).

(1) 10 (2) +1 (3) 10^{-1} (4)–1

10. A solution has pOH equal to 13 at 298 K. The solution will be

(1) Highly acidic (2) Highly basic

(3) Moderately basic (4) Unpredictable

11. What would be $[H^+]$ of 0.006 M benzoic acid ($K = 6 \times 10^{-5}$)

(1) 0.6×10^{-4} (2) 6×10^{-4} (3) 6×10^{-3} (4) 3.6×10^{-4}

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Salts, Types of Salt and Conjugate Theory

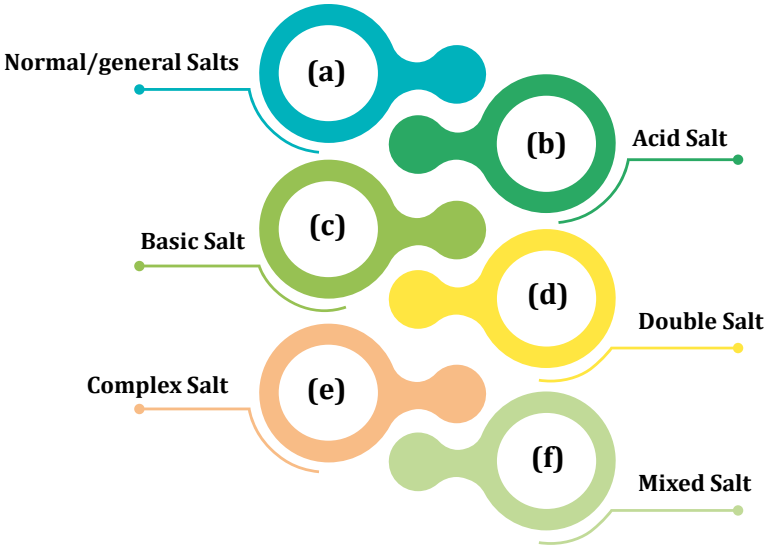
A. **Salt:** Salts are regarded as compounds made up of positive and negative ions. The positive part comes from a base while negative part from an acid. Salts are ionic compounds.

i.e. A compound formed by the neutralization of acid and base is known as salt.

Acid + Base $\rightarrow$ Salt + Water; ΔH = –ve

$HCl + NaOH \rightarrow NaCl$ (Salt) + H_2O

B. **Types of Salt**



(a) **Normal/general salts:** The salts formed by the loss of all possible protons of an acid and all hydroxide ions of base are called normal salts. Such a salt does not contain either a replaceable hydrogen ion or a hydroxyl (OH^-) group.

Ex.: $NaCl$, $NaNO_3$, K_2SO_4, $Ca_3(PO_4)_2$, Na_2HPO_3, NaH_2PO_2 etc.

(b) **Acid salts:** Salts formed by incomplete neutralisation of poly basic acids are called acid salts. Such salts still contain one or more replaceable hydrogen ions (H^+).

Ex.: $NaHCO_3$, $NaHSO_4$, NaH_2PO_4, Na_2HPO_4 etc.

(c) **Basic salts:** Salts formed by incomplete neutralisation of poly acidic bases are called basic salts. Such salts still contain one or more hydroxide ions.

Ex.: $Zn(OH)Cl$, $Mg(OH)Cl$, $Fe(OH)_2Cl$, $Bi(OH)_2Cl$ etc.

(d) **Double salts:** The addition compounds formed by the combination of two simple salts are termed as double salts. Such salts are stable in solid state only i.e. when dissolved in water they break into simple ions.

Ex.: $FeSO_4.(NH_4)_2SO_4.6H_2O$, (Ferrous ammonium sulphate) $K_2SO_4.Al_2(SO_4)_3.24H_2O$ etc. (Potash alum)

(e) **Complex salts:** These salts when dissolved in water give complex ions. Complex ions are stable in solid state as well as in solutions.

Ex.: $K_4[Fe(CN)_6]$, $[Co(NH_3)_6]SO_4$, $[Ag(NH_3)_2Cl$ etc.

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(f) **Mixed salts:** The salts which furnish more than one type of cations or more than one type of anions when dissolved in water are called mixed salts.
These are formed by the neutralisation of more than one acids and bases.

Ex.

H_2SO_4 + NaOH → $NaHSO_4$ + H_2O
Acid Base Acid Salt

NaHSO4 + KOH → $NaKSO_4$ + H_2O
Acid Salt Base Mixed Salt

$CaOCl_2$ NaKS

(a) **Types of general salts:**

(i) SASB (ii) SAWB (iii) WASB (iv) WAWB

Illustration 19:

Which of the following is not an example of an acid salt?

(1) HCOONa (2) NaH_2PO_2 (3) NaHS (4) (1) and (2) both

Solution:

(4)

Illustration 20:

Calculate the no. of ions in Mohr's salt [$FeSO_4.(NH_4)_2SO_4.6H_2O$] or Ferrous Ammonium Sulphate:

Solution:

$FeSO_4.(NH_4)_2SO_4.6H_2O \rightarrow Fe^{+2} + SO_4^{-2} + 2NH_4^+ + SO_4^{-2} + 6\,H_2O$

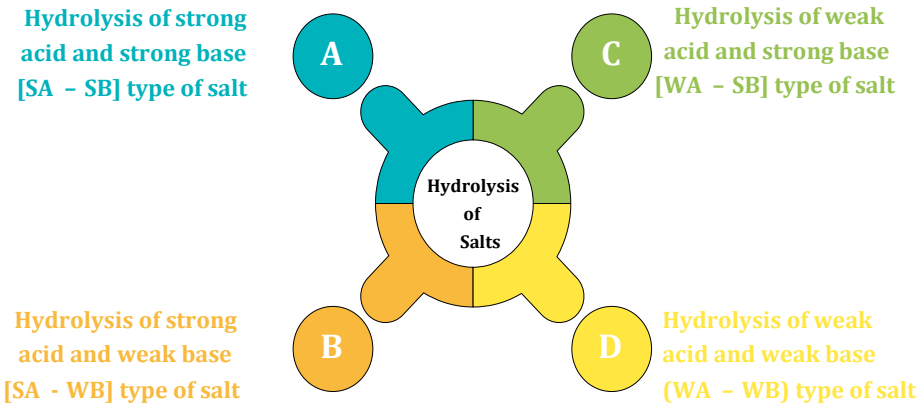
Total number of ions = 5

Hydrolysis of Salts

Salt hydrolysis is defined as the process in which water reacts with cation or anion or both of a salt to change the concentration of H^+ and OH^- ions of water.

Salt hydrolysis is the reverse process of neutralization.

Water + Salt ⇌ Acid + Base ; ΔH = +ve


Hydrolysis of strong acid and strong base [SA – SB] type of salt
A
C
Hydrolysis of weak acid and strong base [WA – SB] type of salt
Hydrolysis of Salts
Hydrolysis of strong acid and weak base [SA - WB] type of salt
B
D
Hydrolysis of weak acid and weak base (WA – WB) type of salt

A. **Hydrolysis of strong acid and strong base [SA – SB] type of salt –**

Ex. NaCl, $BaCl_2$, Na_2SO_4, $KClO_4$, $BaSO_4$, $NaNO_3$, KBr, KCl etc.

$Na^+ + Cl^- + H_2O \longrightarrow Na^+ + OH^- + H^+ + Cl^-$

$H_2O \rightleftharpoons H^+ + OH^-$ (It is not salt hydrolysis)

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(i) Hydrolysis of salt of [SA – SB] is not possible as both cation and anion are not reactive.
(ii) Aqueous solution of these type of salt is neutral in nature. (pH = pOH = 7)
(iii) pH of the solution is 7.
(iv) No effect on litmus paper.

B. Hydrolysis of strong acid and weak base [SA - WB] type of salt –

Ex. $CaSO_4$, NH_4Cl, $(NH_4)_2SO_4$, $Ca(NO_3)_2$, $ZnCl_2$, $CuCl_2$, $CaCl_2$, AgCl, AgI, $AgNO_3$ etc

$$NH_4Cl + H_2O \rightleftharpoons \underset{WB}{NH_4OH} + \underset{SA}{HCl}$$

$$NH_4^+ + Cl^- + H_2O \rightleftharpoons NH_4OH + H^+ + Cl^-$$

$$NH_4^+ + H_2O \rightleftharpoons NH_4OH + H^+$$

(i) In this type of salt hydrolysis, cation reacts with H_2O therefore called as cationic hydrolysis. The cation of the salt which has come from weak base is reactive.
(ii) Solution is acidic in nature as $[H^+]$ is increased.
(iii) pH of the solution is less than 7.
(iv) Solution turns blue litmus paper red.

K_h	=	Hydrolysis constant	K_W	=	Ionic product of water
K_a	=	Ionisation constant of acid	K_b	=	Ionisation constant of base
C	=	Concentration of salt (concentration of ions)	h	=	Degree of hydrolysis

(a) Relation between K_h, K_W and K_b

$$B^+ + H_2O \rightleftharpoons BOH + H^+$$

$$NH_4^+ + H_2O \rightleftharpoons NH_4OH + H^+$$

Hydrolysis constant $[K_h]$

$$K_h = \frac{[NH_4OH][H^+]}{[NH_4^+]} \qquad .....(1)$$

For weak Base $NH_4OH \rightleftharpoons NH_4^+ + OH^-$

$$K_b = \frac{[NH_4^+][OH^-]}{[NH_4OH]} \qquad .....(2)$$

For water $H_2O \rightleftharpoons H^+ + OH^-$

$$K_W = [H^+]\,[OH^-] \qquad .....(3)$$

Now multiplying Eq. (1) and (2) = Eq. (3)

$$\frac{[NH_4OH][H^+]}{[NH_4^+]} \times \frac{[NH_4^+][OH^-]}{[NH_4OH]} = [H^+]\,[OH^-]$$

i.e. $K_h \times K_b = K_W$

$$\boxed{K_h = \frac{K_W}{K_b}} \qquad .....(4)$$

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(b) Degree of hydrolysis – Represented by h

	$NH_4^+ + H_2O$	$\rightleftharpoons$	$NH_4OH +$	H^+
Initial concentration of salt	C		0	0
	C – Ch		Ch	Ch

$$K_h = \frac{[NH_4OH][H^+]}{[NH_4^+]} = \frac{Ch \times Ch}{C - Ch} = \frac{C^2h^2}{C(1-h)} = \frac{Ch^2}{(1-h)}$$

Since $h <<<< 1$ then $(1 - h) \simeq 1$

$$\therefore \quad \boxed{K_h = Ch^2} \qquad \text{.....(5)}$$

$$h^2 = \frac{K_h}{C} \quad \Rightarrow \quad h = \sqrt{\frac{K_h}{C}} \qquad \text{.....(6)}$$

$$\therefore \quad K_h = \frac{K_W}{K_b} \quad \Rightarrow \quad h = \sqrt{\frac{\frac{K_W}{K_b}}{C}}$$

$$h = \sqrt{\frac{K_W}{K_b \times C}} \qquad \text{.....(7)}$$

(c) pH of the solution: $pH = -\log [H^+]$

$$[H^+] = Ch = C\sqrt{\frac{K_W}{K_b \times C}} \quad \Rightarrow [H^+] \sqrt{\frac{K_W \times C}{K_b}} \qquad \text{.....(8)}$$

Taking – log on both sides

$$-\log [H^+] = -\log \sqrt{\frac{K_W \times C}{K_b}}$$

$$\Rightarrow \quad pH = -\log \left(\frac{K_W \times C}{K_b}\right)^{1/2}$$

$$pH = -\frac{1}{2}\,[\log K_W + \log C - \log K_b]$$

$$pH = -\frac{1}{2}\log K_W - \frac{1}{2}\log C - \frac{1}{2}(-\log K_b)$$

$$pH = \frac{1}{2}pKw - \frac{1}{2}\log C - \frac{1}{2}pK_b$$

$$pH = 7 - \frac{1}{2}pK_b - \frac{1}{2}\log C \qquad \text{.....(9)}$$

C. Hydrolysis of weak acid and strong base [WA – SB] type of salt –

Ex. CH_3COONa, $HCOONa$, KCN, $NaCN$, K_2CO_3, $BaCO_3$, K_3PO_4 etc.

$$CH_3COONa + H_2O \; CH_3 \rightleftharpoons \underset{WA}{CH_3COOH} + \underset{SB}{NaOH}$$

$$CH_3COO^- + Na^+ + H_2O \rightleftharpoons CH_3COOH + Na^+ + OH^-$$

$$CH_3COO^- + H_2O \rightleftharpoons CH_3COOH + OH^-$$

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(i) In this type of salt hydrolysis, anion reacts with water therefore called as anionic hydrolysis. The anion of the salt which has come from weak acid is reactive.
(ii) Solution is basic in nature as $[OH^-]$ increases.
(iii) pH of the solution is greater than 7.
(iv) Solution turns red litmus paper blue.

(a) Relation between K_h, K_W and K_a

$CH_3COO^- + H_2O \rightleftharpoons CH_3COOH + OH^-$

$$K_h = \frac{[CH_3COOH][OH^-]}{[CH_3COO^-]} \quad \text{.....(1)}$$

For weak acid

$CH_3COOH \rightleftharpoons CH_3COO^- + H^+$

$$K_a = \frac{[CH_3COO^-][H^+]}{[CH_3COOH]} \quad \text{.....(2)}$$

For water

$H_2O \rightleftharpoons H^+ + OH^-$

$K_W = [H^+]\,[OH^-]$ .....(3)

Now multiply eq. (1) × eq. (2) = eq. (3)

$$\frac{[CH_3COOH][OH^-]}{[CH_3COO^-]} \times \frac{[CH_3COO^-][H^+]}{[CH_3COOH]} = [H^+]\,[OH^-]$$

$K_h \times K_a = K_W$

$$\boxed{K_h = \frac{K_W}{K_a}} \quad \text{.....(4)}$$

(b) Degree of hydrolysis (h):

	CH_3COO^- +	H_2O ⇌	CH_3COOH +	OH^-
Initial concentration of salt	C		0	0
	C – Ch		Ch	Ch

$$K_h = \frac{[CH_3COOH][OH^-]}{[CH_3COO^-]} = \frac{Ch \times Ch}{C - Ch} = \frac{C^2h^2}{C(1-h)}$$

$$K_h = \frac{Ch^2}{(1-h)}$$

Since $h <<<< 1$ then $(1 - h) \simeq 1$

$\therefore$ $\boxed{K_h = Ch^2}$ .....(5)

$$h^2 = \frac{K_h}{C} \quad \text{or} \quad h = \sqrt{\frac{K_h}{C}} \quad \text{.....(6)}$$

$$\boxed{h = \sqrt{\frac{K_W}{K_a \times C}}} \quad \text{.....(7)}$$

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(c) pH of the solution

$[OH^-] = Ch$

$[OH^-] = C \times \sqrt{\frac{K_W}{K_a \times C}}$ or $[OH^-] = \sqrt{\frac{K_W \times C}{K_a}}$ .....(8)

taking – log on both sides

$-\log [OH^+] = -\log \left(\frac{K_w.C}{K_a}\right)^{1/2}$

$pOH = -\frac{1}{2}[\log K_W + \log C - \log K_a]$

$pOH = \frac{1}{2} pK_W - \frac{1}{2} pK_a - \frac{1}{2} \log C$ or $pOH = 7 - \frac{1}{2} pK_a - \frac{1}{2} \log C$

$\because$ $pH + pOH = 14$

$pH = 14 - pOH$

$\therefore$ $pH = 7 + \frac{1}{2} pK_a + \frac{1}{2} \log C$ .....(9)

Illustration 21:

Which of the following solutions has maximum degree of hydrolysis?

(1) 0.1 M NH_4Cl (2) 0.01 M NH_4Cl (3) 0.001 M NH_4Cl (4) Same in all

Solution:

$NH_4^+ + H_2O \rightleftharpoons NH_4OH + H^+$

$K_h = \frac{K_w}{K_b} \Rightarrow h = \sqrt{\frac{K_h}{C}}$

Lower the conc., higher will be degree of hydrolysis.

Ans: (3)

Illustration 22:

Which of the following solutions has maximum pH?

(1) 0.1 M NaCl (2) 0.1 M NH_4Cl (3) 0.001 M NH_4Cl (4) 0.01 M NH_4Cl

Solution:

Salt	**Salt type**	**pH**
NaCl	SASB	7
NH_4Cl	SAWB	<7

$\left[pH = 7 - \frac{1}{2}(pK_b + \log C)\right]$

$\therefore$ NaCl solution has more pH than solution of NH_4Cl.

Ans: (1)

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Illustration 23:

Calculate pH of 10^{-2} M KCN solution if dissociation constant of HCN = 10^{-10}.

Solution:

$K_a = 10^{-10} \Rightarrow pK_a = 10$

$CN^- + H_2O \Rightarrow HCN + OH^-$

$$K_h = \frac{K_w}{K_a}$$

$pH = 7 + ½ (pK_a + \log C)$

$\Rightarrow$ $pH = 7 + ½ (10 + \log 10^{-2}) = 11$

D. Hydrolysis of weak acid and weak base (WA – WB) type of salt :

Ex. CH_3COONH_4, AgCN, NH_4CN, $CaCO_3$, $[NH_4]_2CO_3$, $ZnHPO_3$ etc.

$$CH_3COONH_4 + H_2O \rightleftharpoons \underset{WA}{CH_3COOH} + \underset{WB}{NH_4OH}$$

$$CH_3COO^- + NH_4^+ + H_2O \rightleftharpoons CH_3COOH + NH_4OH$$

* Maximum hydrolysis occurs of the salt of (WA – WB) as both the cation and anion are reactive.
* Solution is almost neutral but it may be acidic or basic depending upon the values of K_a and K_b
* pH of the solution is near to 7.

For WA - WB types of salt

S.No.		$K_a > K_b$	$K_b > K_a$	$K_a = K_b$
1.	Hydrolysis	Cationic-anionic	Anionic-cationic	Neutral hydrolysis
2.	Nature	Acidic	Basic	Neutral
3.	pH	pH < 7	pH > 7	pH =7

(a) Relation between K_h, K_w, K_a and K_b

$$CH_3COO^- + NH_4^+ + H_2O \rightleftharpoons CH_3COOH + NH_4OH$$

$$K_h = \frac{[CH_3COOH][NH_4OH]}{[CH_3COO^-][NH_4^+]} \quad \text{.....(1)}$$

For weak base

$NH_4OH \rightleftharpoons NH_4^+ + OH^-$

$$K_b = \frac{[NH_4^+][OH^-]}{[NH_4OH]} \quad \text{.....(2)}$$

For weak acid

$CH_3COOH \rightleftharpoons CH_3COO^- + H^+$

$$K_a = \frac{[CH_3COO^-][H^+]}{[CH_3COOH]} \quad \text{.....(3)}$$

For water

$H_2O \rightleftharpoons H^+ + OH^-$

$K_W = [H^+][OH^-]$ .....(4)

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Multiply Eq. (1) × Eq. (2) × Eq. (3) = Eq. (4)

$$\frac{[CH_3COOH][NH_4OH]}{[CH_3COO^-][NH_4^+]} \times \frac{[NH_4^+][OH^-]}{[NH_4OH]} \times \frac{[CH_3COO^-][H^+]}{[CH_3COOH]} = [H^+]\,[OH^-]$$

$K_h \times K_b \times K_a = K_W$

$$\boxed{K_h = \frac{K_W}{K_a \times K_b}} \qquad \text{.....(5)}$$

(b) Degree of hydrolysis (h) –

	CH_3COO^-	+ $NH_4^+ + H_2O$	$\rightleftharpoons$	CH_3COOH	+ NH_4OH
Initial concentration of salt	C	C		0	0
	C – Ch	C – Ch		Ch	Ch

$$K_h = \frac{[CH_3COOH][NH_4OH]}{[CH_3COO^-][NH_4^+]} = \frac{Ch \times Ch}{(C-Ch)(C-Ch)} = \frac{C^2h^2}{C(1-h) \times C(1-h)}$$

Since $h <<<< 1$ then $(1 - h) \simeq 1$

$\therefore$ $\boxed{K_h = h^2}$ .....(6)

or $h^2 = \frac{K_W}{K_a \times K_b}$ or $\boxed{h = \sqrt{\frac{K_W}{K_a \times K_b}}}$ .....(7)

(c) pH of the solution

From equation (3)

$$K_a = \frac{[CH_3COO^-][H^+]}{[CH_3COOH]}$$

$$[H^+] = \frac{K_a \times [CH_3COOH]}{[CH_3COO^-]} = \frac{K_a \times Ch}{C-Ch} = \frac{K_a \times h}{1-h}$$

Since $h <<<< 1$ then $(1 - h) \simeq 1$

$[H^+] = K_a \times h$[Now put the value of h from eq. (5)]

$$= K_a \times \sqrt{\frac{K_W}{K_a \times K_b}}$$

$$\boxed{[H^+] = \sqrt{\frac{K_W \times K_a}{K_b}}} \qquad \text{.....(8)}$$

Taking – log on both sides $-\log [H^+] = -\log \left(\frac{K_W \times K_a}{K_b}\right)^{1/2}$

$$pH = -\frac{1}{2}[\log (K_w \times K_a) - \log K_b]$$

$$pH = -\frac{1}{2}[\log K_W + \log K_a - \log K_b]$$

$$pH = -\frac{1}{2}[\log K_W] - \frac{1}{2}[\log K_a] - \frac{1}{2}[-\log K_b]$$

$$pH = +\frac{1}{2}pK_W + \frac{1}{2}pK_a - \frac{1}{2}pK_b$$

$$\boxed{pH = 7 + \frac{1}{2}pK_a - \frac{1}{2}pK_b} \qquad \text{.....(9)}$$

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Illustration 24:

What is the pH of 1 M CH_3COONa solution? K_a of acetic acid = 1.8×10^{-5}, $K_w = 10^{-14}$ $mol^2 L^{-2}$

(1) 2.4 (2) 3.6 (3) 4.8 (4) 9.4

Solution:

(4)

Illustration 25:

Calculate the degree of hydrolysis of a mixture containing 0.1N NH_4OH and 0.1N HCN If $K_a = 10^{-5}$ and $K_b = 10^{-5}$

Solution:

Salt is [WA – WB]

$$h = \sqrt{\frac{K_W}{K_a \times K_b}} = \sqrt{\frac{10^{-14}}{10^{-5} \times 10^{-5}}} = \sqrt{10^{-14} \times 10^{+10}} = \sqrt{10^{-4}} = 10^{-2}$$

Illustration 26:

Assertion : An aqueous solution of NH_4NO_3 is acidic in character.

Reason : NH_4NO_3 in an aqueous solution undergoes anionic hydrolysis.

(1) A (2) B (3) C (4) D

Solution:

(3)

BEGINNER'S BOX-2

1. When sodium acetate (CH_3COONa) is added to aqueous solution of acetic acid (CH_3COOH), the–

(1) The pH value becomes zero (2) pH value remains unchanged

(3) pH value decreases (4) pH value increases

2. Which of the following cations is not hydrolyzed in an aqueous solution ?

(i) Mg^{2+} (ii) Ca^{2+} (iii) Na^{+} (iv) K^{+}

(1) (i), (ii) (2) (iii), (iv) (3) (i), (ii), (iii), (iv) (4) (i), (ii), (iii)

3. Which of the anions is not hydrolyzed in an aqueous solution ?

(i) Cl^- (ii) NO_3^- (iii) Br^- (iv) ClO_4^-

(1) (i), (ii), (iii), (iv) (2) (ii), (iii), (iv) (3) (i), (ii), (iii) (4) (ii), (iv)

4. Which of the following salts does not undergo hydrolysis ?

(1) KCN (2) KCl (3) NH_4NO_3 (4) $FeCl_3.6H_2O$

5. Which of the following salts undergoes anionic hydrolysis ?

(1) $AlCl_3$ (2) $CuSO_4$ (3) Na_2CO_3 (4) NH_4Cl

6. For cationic hydrolysis, pH is given by–

(1) $pH = \frac{1}{2}pK_w + \frac{1}{2}pK_a + \frac{1}{2}\log C$ (2) $pH = \frac{1}{2}pK_w - \frac{1}{2}pK_b - \frac{1}{2}\log C$

(3) $pH = \frac{1}{2}pK_w + \frac{1}{2}pK_a - \frac{1}{2}pK_b$ (4) $pH = \frac{1}{2}pK_w + \frac{1}{2}pK_b + \frac{1}{2}\log C$

7. Which of the following salts is neutral in water ?

(1) KCl (2) NH_4NO_3 (3) NH_4CN (4) NH_4OH

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Buffer Solution

Introduction

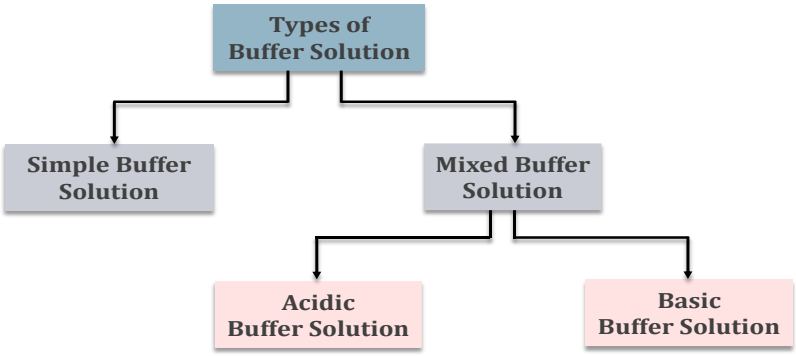
A. **Definition**: A solution which resists the change in pH and whose pH does not change significantly on addition of small amount of strong acid or strong base is called buffer solution.

B. **Properties of buffer solution:**

(i) The pH of buffer solution does not change appreciably upon the addition of small amount of either strong acid or strong base.

(ii) The pH of buffer solution does not depend on the volume of solution. Hence, solution can be diluted without change in pH.

(iii) The pH of buffer solution remains constant even if it is kept for a long time.
Change in pH of a solution occurs due to change in concentration of free H^+ or OH^- ions.



A. **Simple buffer solution :-** Aqueous solution of weak acid-weak base (WA – WB) type of salt.
Ex. CH_3COONH_4, NH_4CN, AgCN etc.

$pH = 7 + \frac{1}{2}pK_a - \frac{1}{2}pK_b$ [pH does not depend on concentration]

$CH_3COO^- + + H_2O \rightleftharpoons CH_3COOH + NH_4OH.$

Case I

When mixing of acid $[H^+]$

$CH_3COO^- + H^+ \rightleftharpoons CH_3COOH$

$NH_4OH + H^+ \rightleftharpoons NH_4^+ + H_2O$

Case II

When mixing of base $[OH^-]$

$NH_4^+ + OH^- \rightleftharpoons NH_4OH$

$CH_3COOH + OH^- \rightleftharpoons CH_3COO^- + H_2O$

B. **Mixed buffer solution :**

(i) **Acidic buffer solution :-** The solution in which weak acid and its conjugate base are present. Or an aqueous solution of mixture of weak acid and salt of same weak acid with any strong base is called as an acidic buffer solution.

Ex. CH_3COOH + CH_3COONa
WA WASB

$CH_3COOH \rightleftharpoons CH_3COO^- + H^+$

$CH_3COONa \rightarrow CH_3COO^- + Na^+$

$\left[\underset{WA}{CH_3COOH} + \underset{C\ Base}{CH_3COO^-}\right] + Na^+$ (Spectator ion)

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Buffer Action:

Case 1. Suppose that a small amount of strong acid is added to the buffer solution. The H^+ ions of the acid react with the basic component, CH_3COO^- ions in the buffer.

$$CH_3COO^-_{(aq)} + H^+ \rightleftharpoons CH_3COOH_{(aq)}$$

Most of the added H^+ ions are consumed because the concentration of CH_3COO^- in the buffer solution is high. The reaction nearly goes to completion because CH_3COOH is a weak acid and its ions have strong tendency to form non-ionized CH_3COOH molecules. Due to the removal of most of the added H^+ ions, there is no appreciable decrease in pH.

Case 2. If a small quantity of strong base is added to the buffer solution, the OH^- ions are consumed by the acidic component CH_3COOH.

$$CH_3COOH_{(aq)} + OH^-_{(aq)} \rightleftharpoons CH_3COO^-_{(aq)} + H_2O_{(\ell)}$$

The effect is the neutralization of most of the added OH^- ions by CH_3COOH. Therefore, there is no appreciable change in pH.

(a) pH of acidic buffer solution :

CH_3COOH + CH_3COONa

Acid + Salt

$CH_3COOH \rightleftharpoons CH_3COO^- + H^+$

$CH_3COONa \rightarrow CH_3COO^- + Na^+$

$$K_a = \frac{[CH_3COO^-][H^+]}{[CH_3COOH]}$$

$$\text{or } [H^+] = \frac{Ka[CH_3COOH]}{[CH_3COO^-]} = \frac{Ka[Acid]}{[Conjugate\,base]}$$

Taking – log on both sides

$$pH = pKa - \log \frac{[Acid]}{[Conjugate\,base]} \text{ or } pH = pKa + \log \frac{[Conjugate\,base]}{[Acid]}$$

Henderson's equation $pH = pKa + \log \frac{[Salt]}{[Acid]}$ or $\frac{[Conjugate\,base]}{[Acid]}$

- $[Conjugate\ base]_{eq} \simeq [Salt]$ because CH_3COO^- mainly comes from salt since dissociation of CH_3COOH in presence of CH_3COONa is appreciably decreased.
- $[Acid]_{eq} \simeq$ initial concentration of acid since it is almost unionised in presence of salt due to common ion effect.

(b) pH range of acidic buffer solution : It depends on pK_a of acid and ratio of salt to acid concentrations.

$$[CH_3COOH] : [CH_3COONa] \Rightarrow pH = pKa + \log \frac{[CH_3COONa]}{[CH_3COOH]}$$

(i) If, $1 : 10 \Rightarrow pH = pKa + \log \frac{10}{1} = pKa + 1$

(ii) If, $10 : 1 \Rightarrow pH = pKa - 1$

So pH range

$$pH = pKa \pm 1$$

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(c) Maximum buffer action condition of acidic buffer solution:

$[CH_3COOH]$: $[CH_3COONa]$

1 : 1 $\Rightarrow$ $pH = pK_a + \log\left(\frac{1}{1}\right)$

Or $pH = pK_a$

(ii) Basic buffer solution :

Definition : The solution in which weak base and its conjugate acid are present. Or an aqueous solution of mixture of weak base and salt of same weak base with any strong acid is called as a basic buffer solution.

Ex. $NH_4OH + NH_4Cl$

$$NH_4OH \rightleftharpoons NH_4^+ + OH^-$$

$$NH_4Cl \longrightarrow NH_4^+ + Cl^-$$

$$\left[\underset{\text{W.B.}}{NH_4OH} + \underset{\text{C.acid}}{NH_4^+}\right] + Cl^- [\text{Spectator ion}]$$

Buffer Action:

Case 1. If a small amount of the strong acid is added to the buffer solution, the H^+ ions are consumed by NH_4OH.

$$NH_4OH_{(aq)} + H^+_{(aq)} \rightleftharpoons NH^+_{4(aq)} + H_2O_{(\ell)}$$

Thus, most of the added H^+ ions are neutralized by NH_4OH and there is no appreciable change in pH.

Case 2. When a small amount of strong base is added to the buffer solution, the OH^- ions react with ions to produce non-ionized NH_4OH molecules.

$$NH^+_{4(aq)} + OH^-_{(aq)} \rightleftharpoons NH_4OH_{(aq)}$$

The concentration of ions is high in the buffer solution. Hence most of the added OH^- ions are consumed. The reaction goes nearly to completion because NH_4OH is a weak base and its ions have strong tendency to form non-ionized NH_4OH molecules. Thus, there is no appreciable increase in pH.

(a) pOH of basic buffer solution :

$[\underset{\text{Base}}{NH_4OH} + \underset{\text{Salt}}{NH_4Cl}]$

$$NH_4OH \rightleftharpoons NH_4^+ + OH^-$$

$$NH_4Cl \longrightarrow NH_4^+ + Cl^-$$

$$K_b = \frac{[NH_4^+][OH^-]}{[NH_4OH]} \quad \text{or} \quad [OH^-] = \frac{K_b[NH_4OH]}{[NH_4^+]}$$

taking – log on both sides $\quad pOH = pK_b + \log\frac{[NH_4^+]}{[NH_4OH]}$

Henderson's equation:

$$pOH = pK_b + \log\frac{[\text{Salt}]}{[\text{Base}]} \text{ or } \frac{[\text{Conjugate acid}]}{[\text{Base}]}$$

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(b) pOH range of basic buffer solution : It depends on pK_b of base and ratio of salt to base concentrations.

$[NH_4OH]$: $[NH_4Cl]$ $\Rightarrow$ $pOH = pK_b + \log\frac{[NH_4Cl]}{[NH_4OH]}$

(i) If, 1 : 10 $\Rightarrow$ $pOH = pK_b + 1$

(ii) If, 10 : 1 $\Rightarrow$ $pOH = pK_b - 1$

So, pOH range : $pOH = pK_b \pm 1$

(c) Maximum buffer action condition of basic buffer solution :

NH_4OH : NH_4Cl $pOH = pK_b + \log\left(\frac{1}{1}\right)$

1 : 1 or $pOH = pK_b$

Buffer Capacity

Definition:

(i) It is defined as the number of moles of strong acid (or strong base) added to one litre of a buffer solution to change its pH by one unit.

(ii) It measures the effectiveness of a buffer.

(iii) Larger the value of buffer capacity more resistant is the solution to pH change.

$$\text{Buffer capacity} = \frac{\text{Number of moles of acid or base added per litre}}{\text{Change in pH of buffer solution}}$$

Illustration 27:

When 2 moles of HCl is added to 1 L of an acidic buffer solution, its pH changes from 3.9 to 3.4. Find its buffer capacity.

Solution:

$$\text{B.C.} = \frac{2}{0.5} = 4$$

Illustration 28:

20 mg of NaOH is added into CH_3COOH solution in which 60 mg of CH_3COOH is present. Calculate the pH of solution if volume of final solution is 10 litre.

[Given $(pK_a)_{CH3COOH} = 4.74$]

Solution:

No. of moles of NaOH $= \frac{20\times10^{-3}}{40} = \frac{10^{-3}}{2}$ mol

No. of moles of CH_3COOH $= \frac{60\times10^{-3}}{60} = 10^{-3}$ mol

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	CH_3COOH	+	$NaOH$	$\rightarrow$	$CH_3COONa + H_2O$
t = 0	10^{-3} mol		$\frac{10^{-3}}{2}$ mol	–	–
$t = t_{eq}$	$\frac{10^{-3}}{2}$		–	$\frac{10^{-3}}{2}$	

Buffer solution is obtained

$$pH = pK_a + \log\frac{[CH_3COONa]}{[CH_3COOH]}$$

$$\Rightarrow pH = 4.74 + \log\left[\frac{10^{-3}}{2\times10} / \frac{10^{-3}}{2\times10}\right]$$

$$\Rightarrow pH = 4.74$$

Illustration 29:

Calculate volume of 0.1 M HCOONa solution that should be added into 50 ml of 0.05 M of HCOOH solution to make a buffer solution of pH = 4. [Given: $pK_a = 3.7$]

Solution:

Suppose 'V' ml volume of HCOONa solution is added then final concentration would be as following:

$$[HCOONa] = \frac{0.1V}{50+V} M$$

$$[HCOOH] = \frac{0.05\times50}{50+V} M$$

$$pH = pK_a + \log\frac{[HCOONa]}{[HCOOH]}$$

$$\Rightarrow 4 = 3.7 + \log\frac{0.1\ V}{0.05\times50}$$

$$\Rightarrow 0.3 = \log\frac{V}{25}$$

$$\Rightarrow \log 2 = \log\frac{V}{25} \Rightarrow \frac{V}{25} = 2 \quad \Rightarrow V = 50 \text{ ml}$$

Illustration 30:

For effectiveness of the buffer solution of CH_3COOH & CH_3COONa, determine its pH range. (pK_a for CH_3COOH = 4.7)

Solution:

pH range of acidic buffer

$\Rightarrow (pK_a - 1 \text{ to } pK_a + 1)$

$= (4.7 - 1 \text{ to } 4.7 + 1)$

$= 3.7 \text{ to } 5.7$

BEGINNER'S BOX-3

1. A buffer solution is one which has–
(1) Reserved acid (2) Reserved base
(3) Constant pH (4) pH equal to 7

2. Which of the following solutions cannot act as a buffer system ?
(1) KH_2PO_4/H_3PO_4 (2) $NaClO_4/HClO_4$
(3) $C_5H_5N/C_5H_5N^+HCl^-$ (4) $Na_2CO_3/NaHCO_3$

3. A buffer solution can not be prepared by mixing equimolar amounts of–
(1) $B(OH)_3$ and $Na_2B_4O_7.10H_2O$ (2) NH_3 and NH_4Cl
(3) HCl and NaCl (4) CH_3COOH and CH_3COONa

4. Which of the following salt solution will act as a buffer ?
(1) CH_3COONH_4 (aq.) (2) NH_4Cl (aq.)
(3) CH_3COONa (aq.) (4) NaCl (aq.)

5. Which of the following combinations will make a buffer solutions ?
(i) CH_3COONa (2 mol) + HCl (1 mol) (ii) CH_3COOH (2 mol) + NaOH (1 mol)
(iii) CH_3COOH (1 mol) + CH_3COONa (1 mol)
(1) (iii) (2) (i), (ii) (3) (ii), (iii) (4) (i), (ii), (iii)

6. The pH of blood circulating in a human body is maintained around 7.4 by the action of the buffer system–
(1) CH_3COOH/CH_3COONa (2) NH_4Cl/NH_3
(3) $H_2PO_4^{2-}$ (4) H_2CO_3/HCO_3^-

Solubility and Solubility Product (K_{sp})

A. Solubility

(a) Definition At constant temperature the maximum number of moles of solute which can be dissolved in a solvent to obtain 1 litre of solution (i.e. saturated solution) is called as solubility.

$$S(mol/L) = \frac{\text{Number of moles of solute}}{\text{Volume of solution (L)}} \qquad S = \frac{X}{M_W \times V_L} \text{ mol } L^{-1}$$

$$S_{g/\ell} = S_{mol/L} \times \text{Molar Mass}$$

B. Solubility Product(K_{sp}):

When a sparingly soluble salt such as AgCl is put into water, a very small amount of AgCl dissolves in water and most of the salt remains undissolved in its saturated solution.

- A solution which remains in contact with undissolved solute is said to be saturated.
- The salt AgCl is an electrolyte, its dissociation occurs in solution. Hence, the quantity of AgCl that dissolves in water dissociates into Ag^+ and Cl^- ions. Thus, in the saturated solution of AgCl an equilibrium exists between undissolved solid AgCl and its ions, Ag^+ and Cl^- ions.

$$AgCl_{(s)} \underset{\text{Precipitation}}{\overset{\text{Dissolution}}{\rightleftharpoons}} Ag^+_{(aq)} + Cl^-_{(aq)}$$

According to law of mass action $K = \frac{[Ag^+].[Cl^-]}{[AgCl]}$

Since, the concentration of undissolved solid AgCl is constant. Thus, the product K [AgCl] gives another constant which is designated as Ksp.

So, K. [AgCl] = $[Ag^+]$. $[Cl^-]$ $\therefore$ $K_{sp} = [Ag^+] . [Cl^-]$

At constant temperature product of concentrations of ions in a saturated solution of substance is called solubility product of that substance. (Saturated solution is that solution in which solid solute and the ions in solution remain in equilibrium with each other.)

- **K_{sp} for $CaCl_2$** $CaCl_2(s) \rightleftharpoons Ca^{+2}(aq) + 2Cl^-(aq)$
  Solubility product in terms of concentration of ions $Ksp = [Ca^{+2}] [Cl^-]^2$
- **K_{sp} for $AlCl_3$** $AlCl_3(s) \rightleftharpoons Al^{+3}(aq) + 3Cl^-(aq)$
  Solubility product in terms of concentration of ions $Ksp = [Al^{+3}] [Cl^-]^3$
- **General form** $AxBy(s) \rightleftharpoons xA^{+y}(aq) + yB^{-x}(aq)$

$$K_{sp} = [A^{+y}]^x [B^{-x}]^y$$

Application of Solubility Product (K_{sp})

(A) To find out the solubility (S) :

(i) K_{sp} of AB type salt

Ex. NaCl, $BaSO_4$, CH_3COONa, $CaCO_3$, NaCN, KCN, NH_4CN, NH_4Cl etc.

$AB(s) \rightleftharpoons A^+(aq) + B^-(aq)$

a	0	0
(a–s)	s	s

$K_{sp} = [A^+] [B^-]$

$$K_{sp} = s^2 \quad \text{or} \quad s = \sqrt{K_{sp}}$$

(ii) K_{sp} of AB_2 or A_2B type salt

Ex. $CaCl_2$, $CaBr_2$, K_2S, $(NH_4)_2SO_4$, K_2SO_4, K_2CO_3 etc.

$AB_2(s) \rightleftharpoons A^{+2}(aq) + 2B^-(aq)$

A	0	0
a – s	s	2s

$K_{sp} = [A^{+2}] [B^-]^2$

$K_{sp} = s \times (2s)^2 = s \times 4s^2 = 4s^3$

$$s = \left(\frac{K_{sp}}{4}\right)^{1/3}$$

(iii) K_{sp} of AB_3 or A_3B type salt

Ex. $FeCl_3$, $AlCl_3$, K_3PO_4 etc.

$AB_3(s) \rightleftharpoons A^{+3}(aq) + 3B^-(aq)$

A	0	0
a–s	s	3s

$K_{sp} = [A^{+3}][B^-]^3 = s \times (3s)^3 = 27s^4$

$$s = \left(\frac{K_{sp}}{27}\right)^{1/4}$$

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(iv) K_{sp} of A_2B_3 or A_3B_2 type salt

Ex. $Al_2(SO_4)_3$, $Ba_3(PO_4)_2$ etc.

$A_2B_3(s) \rightleftharpoons 2A^{+3}(aq) + 3B^{-2}(aq)$

a	0	0
a–s	2s	3s

$K_{sp} = \left[A^{+3}\right]^2\left[B^{-2}\right]^3 = 2s \times 2s \times 3s \times 3s \times 3s = 108s^5$

$$s = \left(\frac{K_{sp}}{108}\right)^{1/5}$$

(v) General form

$A_xB_y(aq) \rightleftharpoons xA^{+y}(aq) + yB^{-x}(aq)$

a	0	0
a–s	xs	ys

$K_{sp} = [A^{+y}]^x . [B^{-x}]^y$

$K_{sp} = (xs)^x . (ys)^y = x^x . y^y . (s)^{(x+y)}$

Illustration 31:

Write the K_{sp} for the following salts.

Solution:

(i) $Al_2(SO_4)_3(s) \rightleftharpoons 2Al^{+3}(aq) + 3SO_4^{-2}(aq)$

$K_{sp} = 2^2 \times 3^3 \times (s)^{2+3} = 4 \times 27 \times s^5 = 108\ s^5$

(ii) $Na_2KPO_4(s) \rightleftharpoons 2Na^+(aq) + K^+(aq) + PO_4^{-3}(aq)$

$K_{sp} = 2^2 \times 1^1 \times 1^1 (s)^{2+1+1} = 4s^4$

(iii) $NaKRbPO_4(s) \rightleftharpoons Na^+(aq) + K^+(aq) + Rb^+(aq) + PO_4^{-3}(aq)$

$K_{sp} = 1^1 \times 1^1 \times 1^1 \times 1^1 \times (s)^{1+1+1+1} = s^4$

Illustration 32:

If solubility product of the base $M(OH)_3$ is 2.7×10^{-11}, the concentration of OH^- will be

(1) 3×10^{-3} (2) 3×10^{-4} (3) 10^{-3} (4) 10^{-1}

Solution:

(1)

Illustration 33:

The solubility of $BaSO_4$ in water is 1.07×10^{-5} mol dm^{-3}. Estimate its solubility product.

Solution:

Solubility equilibrium for $BaSO_4$ is $BaSO_4(s) \rightleftharpoons Ba^{+2}(aq) + SO_4^{-2}(aq)$

The solubility product is, $K_{sp} = [Ba^{2+}] \times [SO_4^{2-}]$

It S is the solubility of $BaSO_4$. then $K_{sp} = S^2$ because x and y = 1.

Now, $S = 1.07 \times 10^{-5}$ M.

Hence, $K_{sp} = (1.07 \times 10^{-5})^2 = 1.145 \times 10^{-10}$

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Illustration 34:

The solubility product of AgBr is 5.2×10^{-13}. Calculate its solubility in mol dm^{-3} and g dm^{-3}. (Molar mass of AgBr. = 187.8 g mol^{-1})

Solution:

The solubility equilibrium of AgBr is $AgBr(s) \rightleftharpoons Ag^+(aq) + Br^-(aq)$

and $K_{sp} = [Ag^+]\,[Br^-] = S^2$ because x = 1 = y.

The molar solubility S of AgBr is given by $s = \sqrt{K_{sp}} = \sqrt{5.2 \times 10^{-13}}$

$s = 7.2 \times 10^{-7} \times 187.8$

$= 1.35 \times 10^{-4}$ g dm^{-3}

(C) Common ion effect on solubility:

Important point:- Solubility of substances always decreases in the presence of common ion. According to Le-Chatelier's principle on increasing common ion concentration equilibrium shifts in backward direction until the equilibrium is re-established, so, the solubility of substances decreases but K_{sp} remains same because it is an equilibrium constant which depends only on temperature.

Illustration 35:

Find out the solubility of AgCl in the presence of C molar NaCl solution ?

Solution:

$AgCl \rightleftharpoons Ag^+ + Cl^-$

s s (Let solubility of AgCl is S mol L^{-1})

$K_{sp} = [Ag^+]\,[Cl^-]$

$K_{sp} = S^2$

In NaCl solution

$NaCl \rightarrow Na^+ + Cl^-$

C C C

Let solubility of AgCl in the presence of NaCl solution is S' mol L^{-1}.

$AgCl \rightleftharpoons Ag^+ + Cl^-$

S' S' S'+C

According to L.M.A.

$K_{sp} = [Ag^+]'\,[Cl^-]'$

$K_{sp} = S'(S' + C) = S'^2 + S'C$ (Neglecting the higher power terms of S')

$K_{sp} = S'\,C$ $\boxed{S' = \frac{K_{sp}}{C}}$

Illustration 36:

Find out the solubility of $CaCl_2$ solution in the presence of C molar NaCl solution?

Solution:

$CaCl_2 \rightleftharpoons Ca^{+2} + 2Cl^-$

S S 2S [Let solubility of $CaCl_2$ is S mol L^{-1}]

$K_{sp} = [Ca^{+2}]\,[Cl^-]^2 = 4S^3$

For NaCl solution

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$NaCl \rightarrow Na^{+} + Cl^{-}$

C C C

Let solubility of $CaCl_2$ in the presence of NaCl solution is S' mol L^{-1}.

$CaCl_2 \rightleftharpoons Ca^{+2} + 2Cl^{-}$

S' S' 2S'+C

According to L.M.A.

$K_{sp} = [Ca^{+2}]' [Cl^{-}]'^{2}$

$K_{sp} = S' (2S' + C)^2 = S' (4S'^{2} + 4S'C + C^2)$

$K_{sp} = 4S'^{3} + 4S'^{2}C + S'C^2$ (Neglecting the higher power terms of S')

$$S' = \frac{K_{sp}}{C^2}$$

Illustration 37:

Find out the solubility of NaCl in the presence of C molar $CaCl_2$ solution ?

Solution:

$CaCl_2 \rightarrow Ca^{+2} + 2Cl^{-}$

C C 2C

Let solubility of NaCl in the presence of $CaCl_2$ solution is S' mol L^{-1}.

$NaCl \rightleftharpoons Na^{+} + Cl^{-}$

S' S' S'+2C

According to L.M.A.

$K_{sp} = [Na^{+}]' [Cl^{-}]'$

$K_{sp} = S' (S' + 2C) = S'^{2} + 2S'C$ (Neglecting the higher power terms of S')

$$S' = \frac{K_{sp}}{2C}$$

(B) Condition of precipitation /Ionic product (IP or Q_{sp}):

- Ionic product (IP) of an electrolyte is defined in the same way as K_{sp}. The only difference is that ionic product expression contains the initial concentration of ions or the concentration at any time whereas the expression of K_{sp} contains only equilibrium concentration. Thus, for AgCl.
  $Q_{sp} = IP = [Ag^{+}]_i [Cl^{-}]_i$ and $K_{sp} = [Ag^{+}]_{eq} [Cl^{-}]_{eq}$
- Ionic product changes with concentration but K_{sp} does not. K_{sp} is applicable for saturated solution of the sparingly soluble electrolyte.
- To decide whether an ionic compound will precipitate, its K_{sp} is compared with the value of ionic product.
  The following three cases arise:

(i) $IP < K_{sp}$	:	The solution is unsaturated and precipitation will not occur.
(ii) $IP = K_{sp}$	:	The solution is saturated and solubility equilibrium exists.
(iii) $IP > K_{sp}$	:	The solution is supersaturated and hence precipitation of the compound will occur.

Thus, a salt is precipitated when its ionic product exceeds the solubility product of the salt.

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(D) Precipitation of soap and salt (NaCl)

(i) Precipitation of NaCl (common salt) :

For the precipitation of NaCl, HCl gas is passed in saturated solution of NaCl to increase the concentration of Cl^- ion by common ion, so ionic product of concentration of Na^+ and Cl^- ion becomes more than K_{sp} of NaCl and NaCl gets easily precipitated.

Saturated solution of NaCl	NaCl	$\rightleftharpoons$	$Na^+ + Cl^-$
	K_{sp}	=	$[Na^+]\,[Cl^-]$
By passing HCl gas	HCl	$\rightarrow$	$H^+ + Cl^-$
due to common ion	K_{sp}	<	$[Na^+]\,[Cl^-]\uparrow$

(ii) Precipitation of soap :

For precipitation of soap, NaCl is mixed in saturated solution of soap to increase the concentration of Na^+ ion by common ion. So ionic product of concentration of Na^+ and stearate ions is more than K_{sp} of soap and soap gets easily precipitated.

Ex. $C_{17}H_{35}COONa$ (Sodium stearate)

Saturated solution of $C_{17}H_{35}COONa$	$C_{17}H_{35}COONa^+$	$\rightleftharpoons$	$C_{17}H_{35}COO^- + Na^+$
	K_{sp}	=	$[C_{17}H_{35}COO^-]\,[Na^+]$
By mixing NaCl solution	NaCl	$\rightarrow$	$Na^+ + Cl^-$
due to common ion	K_{sp}	<	$[C_{17}H_{35}COO^-]\,[Na^+]\uparrow$

Illustration 38:

Solubility of $CaCl_2$ is 4×10^{-8}, then find out its K_{sp} and its new solubility in the presence of 10^{-2} M $Ca(OH)_2$.

Solution:

$CaCl_2 \rightleftharpoons Ca^{+2} + 2Cl^-$

s 2s (Initial solubility = s)

$K_{sp} = 4s^3 = 4(4 \times 10^{-8})^3 = 256 \times 10^{-24}$ .....(i)

$Ca(OH)_2 \rightarrow Ca^{+2} + 2OH^-$

C 0 0

0 C 2C

$CaCl_2 \rightleftharpoons Ca^{+2} + 2Cl^-$

s' +C 2s' (New solubility = s')

$K_{sp} = [Ca^{+2}]'\,[Cl^-]^{2\,'}$

$= [s' + C]\,[2s']^2 = 4s'^3 + 4s'^2C$ (s'^3 = negligible)

$K_{sp} = 4s'^2C$ .....(ii)

From equation (i) and (ii)

$s'^2 = \frac{K_{sp}}{4C} = \frac{256\times10^{-24}}{4\times10^{-2}} = 64 \times 10^{-22}$

$s' = 8 \times 10^{-11}$ mol L^{-1}

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Illustration 39:

Which of the following sets of concentration is responsible for the precipitation of PbI_2 ($K_{SP} = 1.2 \times 10^{-13}$ M)

(1) $[Pb^{2+}] = 10^{-5}$; $[I^-] = 10^{-5}$ M **(2) $[Pb^{2+}] = 10^{-7}$; $[I^-] = 10^{-4}$ M**

(3) $[Pb^{2+}] = 10^{-6}$; $[I^-] = 10^{-5}$ M **(4) $[Pb^{2+}] = 10^{-4}$; $[I^-] = 10^{-4}$ M**

Solution:

(4)

For precipitation

IP > K_{sp}

$K_{sp} = 1.2 \times 10^{-13}$

(1) IP = $[Pb^{+2}]\,[I^-]^2 = 10^{-5} \times (10^{-5})^2 = 10^{-15}$ (2) IP = $10^{-7} \times 10^{-8} = 10^{-15}$

(3) IP = $10^{-6} \times 10^{-10} = 10^{-16}$ (4) IP = $10^{-4} \times 10^{-8} = 10^{-12}$

Illustration 40:

At what pH the precipitation of $Zn(OH)_2$ ($K_{SP} = 1 \times 10^{-12}\ M^3$) will start from the aqueous solution which is saturated with 0.001 M Zn^{2+} ion.

Solution:

$(K_{sp})_{Zn(OH)_2} = 10^{-12}$

$Q_{sp} = K_{sp} = [Zn^{+2}]\,[OH^-]^2$

$Q_{sp} = 10^{-3} \times [OH^-]^2 = 10^{-12}$

$[OH^-]^2 = 10^{-9}$

2 pOH = 9

pOH = 4.5

$\therefore$ pH = 9.5

BEGINNER'S BOX-4

1. The units of solubility product of silver chromate (Ag_2CrO_4) will be–

(1) mol^2L^{-2} (2) mol^3L^{-3} (3) $mol\ L^{-1}$ (4) $mol^{-1}L$

2. At a certain temperature, the solubility of the salt A_xB_y is S moles per liter. The general expression for its solubility product will be–

(1) $K_{sp} = x^y y^x S^{x+y}$ (2) $K_{sp} = (xy)^{x+y} S^{x+y}$ (3) $K_{sp} = (x^x y^y) S^{x+y}$ (4) $K_{sp} = x^x y^y S^{xy}$

3. The molar solubility of silver sulphate is 1.5×10^{-2} mol L^{-1}. The solubility product of the salt will be–

(1) 2.25×10^{-4} (2) 1.35×10^{-5} (3) 1.7×10^{-6} (4) 3.0×10^{-3}

4. The precipitate of CaF_2 ($K_{sp} = 1.7 \times 10^{-10}$) is obtained when equal volumes of the following are mixed:

(1) 10^{-3} M Ca^{2+} + 10^{-5} M F^- (2) 10^{-5} M Ca^{2+} + 10^{-3} M F^-

(3) 10^{-2} M Ca^{2+} + 10^{-3} M F^- (4) 10^{-4} M Ca^{2+} + 10^{-4} M F^-

5. If S_0, S_1, S_2 and S_3 are the solubilities of AgCl in water, 0.01 M $CaCl_2$, 0.01 M NaCl and 0.5 M $AgNO_3$ solutions, respectively, then which of the following is true?

(1) $S_0 > S_2 > S_1 > S_3$ (2) $S_0 = S_2 = S_1 > S_3$ (3) $S_3 > S_1 > S_2 > S_0$ (4) $S_0 > S_2 > S_3 > S_1$

6. Given K_{sp} (AgI) = 8.5×10^{-17}. The solubility of AgI in 0.1 M KI solution is–

(1) 0.1 M (2) 8.5×10^{-16} M (3) 8.5×10^{-17} M (4) 8.5×10^{-18} M

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Acid and Base

Introduction

The earliest classification of substances into acids and bases was based upon the characteristic properties possessed by each one of them. For example,

Acid was defined as a substance whose aqueous solution possesses the following characteristic properties:

(i) conducts electricity.

(ii) reacts with active metals like zinc, magnesium etc. to give hydrogen.

(iii) turns blue litmus red.

(iv) has a sour taste.

(v) whose acidic properties disappear on reaction with a base.

Base was defined as a substance whose aqueous solution possessed the following characteristic properties:

(i) conducts electricity,

(ii) reacts with active metals like zinc, magnesium etc. to give hydrogen,

(iii) turns red litmus blue,

(iv) has a bitter taste

(v) whose basic properties are destroyed on reaction with an acid.

The above definitions of acids and bases are called operational definitions as they are based on certain operations (i.e. tests) to be performed on the substances. However, these have been replaced by conceptual definitions (put forward by Arrhenius, Bronsted-Lowry and Lewis) which go into the causes of the observed behavior, based upon structure and composition of the substances.

Arrhenius Concept (1884)

(a) Acid:- According to this concept, those substances which produce free H^+ ions in aqueous solution are called acids.

Example

HCl, HNO_3, H_2SO_4, H_3PO_4, H_2CO_3, H_2S, CH_3COOH etc.

$HCl + H_2O \rightarrow H^+(aq.) + Cl^-(aq.)$

$H_2SO_4 + H_2O \rightarrow 2H^+(aq.) + SO_4^{-2}(aq.)$

$CH_3COOH + H_2O \rightleftharpoons CH_3COO^-(aq.) + H^+(aq.)$

(b) Base:- Those substances which produce free OH^- ions in aqueous solution are called bases.

Example

$NaOH$, KOH, $Cs(OH)$, $Rb(OH)$, NH_4OH, $Ba(OH)_2$, $Ca(OH)_2$, $Al(OH)_3$ etc.

$NaOH + H_2O \rightarrow Na^+(aq.) + OH^-(aq.)$

$Ba(OH)_2 + H_2O \rightarrow Ba^{+2}(aq.) + 2OH^-(aq.)$

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(c) Nature of water:- According to this concept nature of water is neutral and act as a solvent.

(d) Neutralisation Reaction :- Those reactions in which acid and base react together to form water molecule are called neutralisation reactions.

i.e. $Na^+ + OH^- + H^+ + Cl^- \rightarrow NaCl + H_2O$

$H^+ + OH^- \rightarrow H_2O$

(e) Strength of acids and bases:- This concept explains the strength of acids and bases depending upon the basis of degree of ionisation.

Example

For strong electrolytes $\alpha \simeq 100\%$

For weak electrolytes $\alpha < 100\%$

(f) Advantage :- This concept explains the acids and bases practically. i.e. to find out the pH, ionisation constant, hydrolysis constants, heat of neutralisation etc.

(g) Disadvantage :-

(i) It explains the behaviour of acids and bases only in aqueous (water) solvents.

(ii) It does not explain the stability of proton (H^+).

Illustration 41:

Gaseous hydrogen chloride is a very poor conductor of electricity but a solution of hydrogen chloride in water is a good conductor. This is due to the fact that :-

(1) Water is a good conductor of electricity

(2) Hydrogen chloride ionises in water

(3) A gas cannot conduct electricity but a liquid can

(4) HCl does not obey Ohm's law where as the solution does

Solution:

(2)

Illustration 42:

Which is acid in the following pairs according to Arrhenius concept ?

(1) HCl(g) and HCl (aq) (2) $CH_3COOH(l)$ and $CH_3COOH(aq)$

Solution:

(1) HCl(aq.) (2) $CH_3COOH(aq.)$

Bronsted-Lowry Concept (1923)

It is based upon the exchange of proton.

(a) Acid :- According to this concept those substances which have tendency to donate proton (H^+) by any method in any solvent are called acids.

Example

(i) $HCl, HNO_3, H_2SO_4, H_2CO_3, H_2S, CH_3COOH, H_3PO_3$ etc. (neutral molecules)

(ii) $HS^-, HCO_3^-, HSO_4^-, H_2PO_4^-, HPO_4^{-2}$ etc. (Anions)

(iii) $NH_4^+, H_3O^+, PH_4^+, CH_3COOH_2^+$ etc. (Cations)

(iv) $[Al(H_2O)_6]^{+3}, [Ag(H_2O)_2]^{+1}, [Fe(H_2O)_6]^{+3}$ etc.

(v) HCl (Acid) + H_2O (Solvent) $\rightarrow$ $H_3O^+ + Cl^-$

(vi) NH_4^+ (Acid) + H_2O (Solvent) $\rightarrow$ $NH_3 + H_3O^+$

(vii) $[Al(H_2O)_6]^{+3}$ (Acid) + H_2O (Solvent) $\rightarrow$ $[Al(H_2O)_5OH]^{+2} + H_3O^+$

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(b) Base :- Those substances which have tendency to accept proton by any method in any solvent are called the bases.

Example

(i) NaOH, KOH, Rb(OH), Cs(OH), $Ba(OH)_2$, $Ca(OH)_2$, NH_4OH, $Al(OH)_3$ etc.

(ii) HS^-, HCO_3^-, HSO_4^-, $H_2PO_4^-$, HPO_4^{-2} etc.

(iii) NH_3, RNH_2, R_2NH, R_3N, $C_6H_5NH_2$, C_5H_5N, $H_2N\text{-}NH_2$ etc.

(iv) O^{-2}, SO_4^{-2}, CO_3^{-2}, Cl^-, Br^-, I^-, CN^- etc.

(v) NH_3 (Base) + H_2O (Solvent) $\rightarrow$ $NH_4^+ + OH^-$

(vi) CO_3^{-2}(Base) + H_2O (Solvent) $\rightarrow$ $HCO_3^- + OH^-$

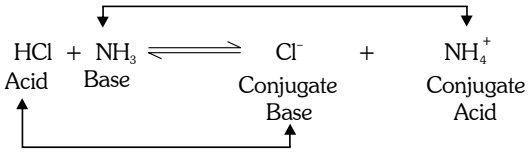
(c) Nature of water :- According to this concept nature of water is amphoteric or amphiprotic i.e. water can act as both acid and base.

(i) HCl (Acid) + H_2O (Base) $\rightarrow$ $Cl^- + H_3O^+$

(ii) NH_3 (Base) + H_2O (Acid) $\rightarrow$ $NH_4^+ + OH^-$

(d) Neutralisation Reaction :- According to this concept those reaction in which acid and base react together and convert into their respective conjugate acid and base are called neutralisation reactions.

Example



(e) Strength of acids and bases :- This concept explain the strength of acid and base depending upon the basis of relative tendency to accept or donate the proton.

(i)	$HClO_4$	(ix)	H_3PO_4	(xvii)	$C_2H_5 - OH$
(ii)	HI	(x)	HF	(xviii)	$CH \equiv CH$
(iii)	HBr	(xi)	CH_3COOH	(xix)	NH_3
(iv)	H_2SO_4	(xii)	H_2CO_3	(xx)	$R–NH_2$
(v)	HCl	(xiii)	H_2S	(xxi)	CH_4
(vi)	HNO_3	(xiv)	NH_4^+	(xxii)	H_2
(vii)	H_3O^+	(xv)	HCN		
(viii)	HSO_4^-	(xvi)	H – OH		

Example

(i) $HCl + H_2O \rightleftharpoons Cl^- + H_3O^+$

Strong acid — Strong base — Weak base — Weak acid

(ii) $HCl + CH_3COOH \rightleftharpoons Cl^- + CH_3COOH_2^+$

Weak acid — Weak base — Strong base — Strong acid

(iii) $HCl + C_6H_6$ (Solvent) $\rightleftharpoons$ HCl does not act as acid because C_6H_6 is an aprotic solvent.

Illustration 43:

Which of the following behave both as Bronsted acid as well as Bronsted bases ?

H_2O, HCO_3^-, H_2SO_4, H_3PO_4, HS^-, NH_3

Solution:

H_2O, HCO_3^-, HS^-, NH_3

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Illustration 44:

Assertion : Cl^- is weaker base than C_2H_5OH.

Reason : Cl^- is conjugate base of stronger acid, HCl.

Solution:

(1)

Lewis Concept (1939)

(a) Lewis Acid:- According to this concept those species which have self tendency to accept the lone pair of electrons are called acids. i.e. Lewis acid is an electron pair acceptor (electrophilic).

(b) Lewis Base:- Those species which have self tendency to donate the lone pair of electrons are called bases. i.e. a base is an electron pair (lone pair) donor (nucleophile).

BEGINNER'S BOX-5

1. Which of the following is a Bronsted acid ?

(i) HCN (ii) $H_2PO_4^-$ (iii) NH_4^+ (iv) HCl

(1) (i), (iii) (2) (i), (ii), (iii), (iv) (3) (ii), (iii) (4) (i), (iii), (iv)

2. Which of the following is a Bronsted base ?

(i) NH_3 (ii) CH_3NH_2 (iii) HCO_3^- (iv) SO_4^{2-}

(1) (i), (ii), (iii), (iv) (2) (i), (ii) (3) (i), (ii), (iii) (4) (i), (iii), (iv)

3. The conjugate base of hydroxide ion is–

(1) H_2O (2) H_3O^+ (3) O^{2-} (4) O_2

4. The conjugate acid of amide ion (NH_2^-) is–

(1) N_2H_4 (2) NH_2OH (3) NH_4^+ (4) NH_3

5. Which of the following can act both as a Bronsted acid as well as a Bronsted base ?

(1) H_2SO_4 (2) HCO_3^- (3) O^{2-} (4) NH_4^+

6. Which of the following acid-base reactions cannot be explained by the Bronsted theory ?

(1) $CO_2 + CaO \longrightarrow CaCO_3$ (2) $BF_3 + NH_3 \longrightarrow \bar{B}F_3\overset{+}{N}H_3$

(3) $Ni + 4CO \longrightarrow Ni(CO)_4$ (4) All of these

7. Which of the following Bronsted acid has the weakest conjugate base ?

(1) H_2O (2) HCN (3) HCOOH (4) HF

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BEGINNER'S BOX — ANSWERS KEY

BEGINNER'S BOX-1	Que.	1	2	3	4	5	6	7	8	9	10
	Ans.	3	1	3	4	1	1	4	4	2	1
	Que.	11									
	Ans.	2									

BEGINNER'S BOX-2	Que.	1	2	3	4	5	6	7
	Ans.	4	2	1	2	3	2	1

BEGINNER'S BOX-3	Que.	1	2	3	4	5	6
	Ans.	3	2	3	1	4	4

BEGINNER'S BOX-4	Que.	1	2	3	4	5	6
	Ans.	2	3	2	3	1	2

BEGINNER'S BOX-5	Que.	1	2	3	4	5	6	7
	Ans.	2	1	3	4	2	4	4